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SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

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Second Quarterly Report

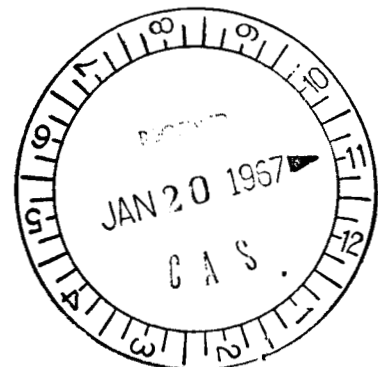
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HEAT STERILIZABLE BATTERY SEPARATORS

Second Quarterly Report

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1. INTRODUCTION

This is the second quarterly report on JPL Contract No. 951525, "Separator Development for a Heat Sterilizable Battery", covering the period October 1 to December 31, 1966. The effort on this contract falls into two areas:

(1) The major part of the work is aimed at producing composite separators for silver-zinc batteries. These composite materials would have a porous organic matrix or binder filled with inorganic substances having ion exchange properties.

(2) A secondary effort aims at modification of macroporous and microporous organic matrices by attachment of chelating functional groups. The work on this part has concentrated on incorporation of 8-hydroxyquinoline groups into epoxy resin matrices.

All of this work is directed toward separators for silver-zinc batteries. The requirements for other types of alkaline batteries have not been considered. The First Quarterly Report (June 1 to September 30, 1966) lists the functions and desirable properties for separators in silver-zinc batteries that must be subjected to sterilization heat treatment. The First Quarterly Report also gives the results of tests in which a large number of candidate organic polymeric materials and possible inorganic filler materials were screened for resistance to hot and cold 40% KOH solutions.

The present report describes progress in the following areas:

(1) membrane fabrication by a number of different techniques; (2) properties of membranes, including effects of solvent and filler on resistivity, the effects of sterilization exposure, and the resistance of composite membranes to penetration by zinc dendrites; (3) evaluation of epoxy resins containing 8-hydroxyquinoline groups; (4) and study of the effects of electrode rotation on dendritic growth of zinc. Details of progress are given in the following sections of the report.

2. MEMBRANE FABRICATION

2.1. Evaporation of solvent by heat

Many additional membranes have been fabricated using a polymer dissolved in a solvent as the binder and an inorganic ion exchange material in powder form as the filler. The binder and filler were hand mixed in different ratios, with the filler being the major portion of the total weight of polymer and filler. Webril, a non-woven polyethylene felt, was used as a supporting and reinforcing structure. The resistivities of some of these films are shown in Table I. This table also gives the percent of polymer and filler, compared to the total weight of the resulting film. Polysulfone in DMAC was mainly used as the binding polymer solution. The fillers were zirconium oxide, titanium oxide, calcium oxide and Linde Molecular Sieve materials. As can be seen, some of these films fell into the required resistivity range. Selected membranes were exposed to sterilization conditions without loss of permeability and without visible change in dimensions or appearance on microscopic observation. However, the distribution of filler material in these separators was non-uniform, as is evident from the photomicrographs shown in Figs. 1 and 2. These inhomogeneities were also apparent from the considerable variations of resistance measurements. Experiments were therefore undertaken in an attempt to produce better filler distributions in cast films.

A number of membranes were prepared by casting on a glass plate. In this preparation method, the polymer solvent was evaporated by application of heat. It was soon noticed that such films are usually glossy on the side peeled from the glass plate and relatively rough on the side exposed to the air. Microscopic examination revealed a non-uniform distribution of the filler. Also, the average resistivity of even the thinnest films was too high to be acceptable and large variations were observed when the resistivity was measured at different places on the film. Sometimes resistivity values differing by a factor of three were noticed.

A considerable improvement in filler distribution was obtained by grinding or ball milling the mixture for a short time, giving better wetting and breaking up of lumps. No wetting agent was added, since the binder-solvent seemed to disperse the filler quite well. This method produced films which had a much smoother appearance and more uniform filler distribution, but they were still quite high in resistivity.

In order to reduce the resistivity, various amounts of cane sugar or polyvinyl alcohol solution were added to the binding resin solution. These materials were used as saturated solutions in DMAC. After drying in an oven at 110°C, the films were then boiled in water to extract the soluble components. This procedure should produce a microporous structure which would be more permeable to KOH, thus decreasing the resistivity. Although the resistance of these films was, in general, slightly lowered, the soluble additives had an adverse effect on the distribution of the filler. Very often the filler separated into small islands, leaving regions containing no filler. Segregation of the filler also occurred at places where there was a temperature gradient during the heating, such as the points where the glass slide rested on supports in the oven. For these reasons, other methods were tried for extraction of the solvent from the cast films.

2.2. Extraction of solvent by water

More satisfactory films were obtained by casting on a glass surface, followed by extraction of the solvent from the still-wet films by immersion in an excess of water or dilute acetic acid. Films could be produced without, or with, filler. The films had an opaque milky appearance. The distribution of the filler remained quite uniform without any sign of segregation. The temperature of the extracting water was varied from 0°C to 90°C. The films did not form when the slide was immersed in very hot water, since the substance on the glass disintegrated before it coagulated into a solid film. On the other hand, the films processed in ice water were similar in appearance and resistivity to the ones produced in water at room temperature.

Films of even better appearance were obtained when the solvent was extracted with 50% acetic acid. These films were, in the average, somewhat thinner and had a glossy appearance even on the air side. They also had a lower resistance, in some instances, than did similar films produced by water extraction.

It may be mentioned that the mixing procedure, which consisted of grinding or ball milling the filler with the binder solution, produced many air bubbles in the mix. These bubbles had a very slow rise time when a viscous polysulfone-DMAC solution was used (for example, 20 g resin to 100 ml DMAC). Sometimes the bubbles did not completely dispel before the film on the glass became partly solidified by partial evaporation of the solvent, thus creating large voids in the finished film after the remainder of the solvent was extracted. Most of these films were therefore prepared from less concentrated solutions. However, as will be indicated below, too dilute solutions produced another effect, of making the films too spongy.

The process of fabrication by water extraction is shown in Figs. 3 and 4. With this new method of casting, experiments were then designed to determine which of the several possible binders is most suitable for membrane fabrication.

2.3. Binder selection

A series of films was prepared both with and without zirconium hydroxide as a filler and with dimethylacetamide (DMAC) as the solvent for the polymer binder. The films were self-supporting. In other instances they were coated on Webril polypropylene mesh as a reinforcing structure. The following polymers were tried as binder: polysulfone, phenoxy, polyvinylidene fluoride, and polyphenylene oxide. All the films were carried through the prescribed sterilizing cycle in hot KOH solution.

The results are shown in Table II and can be summarized as follows:

(1) Polysulfone produced a mechanically strong membrane either unsupported or supported on Webril, with little weight loss and with preservation of dimensional stability.

(2) Phenoxy (poron) has a low softening point which is around 100°C and stable films could only be prepared with a support of Webril.

(3) Polyvinylidene fluoride darkens in the cycling process, forming a brittle powdery film.

(4) For the preparation of the polyphenylene oxide polymer film, a slightly different fabrication procedure was used because of the insolubility of this polymer in DMAC. A double extraction procedure was employed. The polymer was dissolved in toluene. The Webril base was saturated with this toluene solution and then the toluene was removed by DMAC. The DMAC was next extracted from the structure by immersion in water, which precipitated the polymer. The resulting film was white and powdery and was quite brittle.

As a result of these experiments, it was decided to use polysulfone in further separator fabrication. Polysulfone can be easily processed from a solvent solution and has the physical strength and chemical stability to withstand the cycling procedure. The incorporation of the filler caused no visible changes in behavior.

3. MEMBRANE PROPERTIES

3.1. Effect of solvent on thickness and resistivity

A series of unfilled, water-extracted, polysulfone-DMAC films was prepared by casting on glass without any reinforcing support. The thickness of the wet film, as cast, was determined by the use of a Gardner Ultra Applicator. This device consists of a metal blade which slides parallel to the glass plate, and which can be set at definite separation distances from the plate. Extraction of the film with water, followed by drying, would be expected to alter this initial thickness. We have investigated the final thickness of films, after extraction and air-drying at room temperature, as a function of the Gardner blade setting and the initial polysulfone concentration in DMAC. Fig. 5 presents these results graphically. The thickness of the dry film is seen to be more dependent on the Gardner blade setting than upon the polysulfone concentration. Very roughly speaking, the dry films have about half the thickness of the Gardner blade setting. This result gives an approximate guide for production of films of a desired thickness.

The data of Fig. 5 indicate that less dense, more spongy films are apparently cast from polymer solutions containing more of the solvent. Microscopic observations showed that the films prepared from dilute solutions consist of small cellular compartments, whereas those made from more concentrated binder solutions are seen to be more compact. Fig. 6 shows a photomicrograph of the cross section of a membrane prepared without filler.

Some of the films obtained by the method just described were soaked in 40% KOH under vacuum and the electrical resistivity determined by a simplified d.c. method described in Appendix I. The results are indicated in Fig. 7. Here it can be seen that the solid to solvent ratio has a pronounced influence on resistivity. Film thickness seems to be of only secondary importance. For a membrane prepared from a solution of 10 g polymer in 100 ml DMAC the resistance was practically the same if the measurements were made on a 2 mil or a 5 mil thick film. By increasing the solid content of the solution the resistance was much higher for the same thickness. This indicates

that the more dense films cannot soak up as much electrolyte as the less dense films apparently can. The resistance values were obtained with a 1/4" round aperture of 0.316 cm² area. Each point in the graph is an average of several determinations. Since films formed from 10 g/100 ml solutions were relatively weak in mechanical strength, it was decided to study the effect of the filler using solutions containing 15 g polysulfone to 100 ml DMAC. The resistivity of any of these films, without filler, is much too high to fall into the acceptable region for battery separators.

3.2. Effect of filler on thickness and resistivity

Films were prepared by ball milling the filler with the solution of polysulfone in DMAC. In these experiments, the same weight percent of filler was always used regardless of its composition. (Five grams of filler was used for each preparation.) Fig. 8 shows that the different fillers have only a secondary effect on the thickness of the film. Here again the resulting dry film thickness depended mainly on the blade setting, the dry thickness being again about half of that of the wet uncoagulated film on the glass slide.

Electrical resistivities for films containing fillers were determined. The films were soaked as usual in 40% KOH under vacuum for 2 days and in the wet form tested for resistivity. These films were first tested by an a.c. method. High resistance values were observed, which fell outside the limit of the apparatus. Surprisingly, much lower resistivity values (sometimes by a factor of 10) were obtained when the measurements were repeated, using the d.c. method. When the same films were once again measured with the a.c. resistance tester, values of resistivity were observed which were much lower than first observed by the a.c. method. This phenomena was at first completely inexplicable. It was thought that it might be associated with the passage of d.c. current. But the low resistivity was also observed on other areas not exposed to the d.c. current so that another explanation was necessary. It finally became apparent that this effect could be associated with the pressure on the film. Since these films are pressed between flat flanges of considerable size, low resistance can be noticed over a wide area. The effect on the filler impregnated films seems to be correlated with known dilatency behavior of

sand. When sand which has been well shaken down is compressed, the grains are redistributed from their equilibrium position in such a way that the net effect is an increase in volume they occupy, thus the density of the structure is reduced. Because of the increased volume in our case, additional electrolyte could soak into the structure, thus decreasing the resistance. That the pressure on the film is responsible for a decrease in resistivity was proven by pressing the film in a hydraulic press. Since the influence of pressure seems to change permanently the resistivity of the films, another explanation could also be put forward. The walls of the tiny cells forming the spongy structure of the film, resulting from the fast extraction of solvent by water, might be permanently damaged by the pressure. If enough of walls are broken, a more interconnected structure will be obtained, with a corresponding lowering in resistance. Since the influence of pressure was first recognized near the end of the series of runs, the values which are given in this report represent the effect of an unknown pressure on the film, resulting from tightening of some winged screws on the tester to prevent the leakage of the electrolyte. The relation of the magnitude of pressure to resistivity has not yet been investigated.

Fig. 9 represents the results with zeolon as filler. Films of different thickness were tested and usually 5 measurements selected for random areas of the film were made. The points obtained are scattered, showing a wide variation of resistivity from place to place on the film. A factor of 2 seems to be not unusual for the extreme values. But there does seem to be a definite trend when one takes into account the average values, namely that the resistivity is increasing with increasing thickness. Fig. 9 also indicates that most of the values fall above the dashed line representing the limit of resistivity for the acceptable value of $150 \Omega\text{-cm}$ if measurements are made with a $1/4$ " aperture. If the values of resistivity are plotted instead for the dry film thickness against the thickness obtained when the film is wet, a more favorable result, although still too high, is obtained.

The results for films prepared from titanium oxide as filler are not as favorable as with zeolon H (Fig. 10). Considerably higher resistances are found which deviate appreciably from the acceptable value of 150Ω -cm indicated by the dashed line. It can be seen that there is considerable scatter in the points. Whether these points, as the average of five measurements, represent the actual inhomogeneity in the films or are the result of pressure influence cannot be stated.

Somewhat better resistivities were obtained by using hydrated zirconium oxide as filler (Fig. 11). The values are quite scattered, but some of the averages fall below the prescribed limit of resistivity. Again the uncertainty of the effect of pressure on these results is not known. An enlarged cross section of a zirconium hydroxide filled film is shown in Fig. 12.

The resistivity of a film produced by spreading the filler and binder on 3 mil Webril is shown in Fig. 13. Zeolon H was again the filler. These measurements do not show as much scatter as was observed for the unsupported films. All the measurements are below the limit set for the proper functioning as a battery separator. The thickness was measured several times and the limits are indicated by the line between arrows. The thicker film shows a variation of about 10%. Both resistivity and thickness were measured at random points.

3.3. Behavior of membranes on sterilization testing

Selected membranes have been cycled in hot KOH and the results are shown in Table III. These data indicate that in the sterilization process an almost complete filler extraction takes place. This result is not too surprising. Testing of zirconium oxide, for example, has revealed that the solubility is about 60 mg in 100 ml KOH at room temperature. Since the total sample weight is 30 mg and a large volume of KOH was used (40 ml) all of the filler should dissolve in the solution. To prevent such dissolution, additional testing was performed in a solution already saturated with the filler which is added in excess to the electrolyte. Whether such a procedure is also permissible in a silver zinc battery is debatable. The experiments have indicated that in some cases little or no filler was extracted under these conditions.

The amount of filler remaining after cycling in hot KOH solution was determined by heating weighed samples of the membranes to a high enough temperature in air to destroy the organic matter. For comparison, samples of films which had not been exposed to hot KOH were also ashed. Additional companion runs were carried out on films not containing added filler. Data are given in Table IV. The results show that less than 0.05% ash remains from ashing the polysulfone alone, and about 0.5% residue is picked up from the necessary ball milling (porcelain No. 000 mill) used to mix polymer solution and filler. The residues remaining from filled membranes not exposed to hot KOH solution fall in the range 18 to 24% (from membranes containing 5 g filler and 15 g polymer). The fact that almost the entire filler material was extracted by the hot KOH solution during the cycling runs indicates that the film structure must be porous with little filler being completely encased in the polysulfone polymer matrix.

3.4. Zn dendrite penetration through separators

It is well known that the successful application of the silver-zinc cell as a secondary battery was made possible by wrapping the silver and zinc electrode in cellophane, with several cycles obtainable through use of multiple layer wraps. Further extension of cycle life was achieved by limiting the discharge to less than 50% of battery capacity and by improving the composition of the separator. Modified cellulose or new permeable classes of resins were developed. These new materials are also more resistant to the degrading action of the silver oxides. The requirement for sterilization adds another factor to the still unsolved problem of dendrite penetration in the silver zinc storage battery.

Although not required by the contract, testing facilities were constructed to determine the resistance of membranes to dendrite penetration. The description of an instrument as given by Dalin and Solomon* was used as a guide in the present investigation. The test consists of determining the

*J. E. Cooper and A. Fleischer, editors. (Air Force Aero Propulsion Labs. 1965). Chapter 12, "Zinc Penetration" by G. A. Dalin and F. Solomon.

time necessary for the dendrite to develop a conductive path through the separator between the zinc electrode as cathode and a non-active sensing electrode in the form of a metallic net located on the other side of the separator. In the arrangement, a zinc electrode is also used as the anode, thus eliminating the depletion of zinc ions in the electrolyte solution during plating. Also, any effect of dissolved silver ions is avoided, which would not be the case if the test were to be made directly in a silver-zinc cell.

A high purity zinc sheet, abraded with fine steel wool, was used for both electrodes. The fine scratches should facilitate dendritic growth. In the design (Fig. 14) the zinc area was marked out with a rubber spacer with a 3/4" diameter hole. In this way no edge of the zinc plate was exposed to the electrolyte. Usually enhanced dendritic growth occurs on an edge. Small holes were drilled on top and bottom of the exposed zinc surface. These holes were to allow the electrolyte to communicate with a compartment in back of the plate, and to permit the escape of any gas generated at the electrode surface. Since the zinc dendrites also grow on this side, opposite facing the anode, the surface was masked by painting with epoxy resin. Also, the holes were lined with polyethylene tubing to prevent dendrite growing on the edges.

The membrane itself was at a distance of 25 mils from the surface of the zinc plate, and in order to keep this distance, even with a separator which would crinkle in the electrolyte, the space was filled with a spacer of 25 mil glass mat of very high porosity. On top of the separator was placed a platinum net of 52 mesh gauze then another rubber gasket and a barrel filled with 40% KOH saturated at room temperature with ZnO. The anode was in the form of a cylinder. Visual inspection of the platinum gauze was possible. A high impedance electrometer (Keithley 200B) was used as the sensing electrometer for registering shorts between the zinc cathode and the platinum gauze. The output of the electrometer was registered on a recorder. The current through the cell was supplied by a variable constant current

power supply, well filtered. The potential of the sensing electrode was between 0.5 to 1.5 volts. When a dendrite penetrated, a considerable voltage drop occurred. Very often this step was not well defined, but rather the voltage declined gradually over an appreciable time, or else had an oscillatory nature so that it was difficult to decide precisely when dendritic penetration had occurred.

Usually microscopic examination was carried out on each membrane in order to determine the extent of dendrite penetration. It could be observed that the dendrites do not pierce the separator but grow into and inside of the structure. The pattern of penetration seems to be characteristic for certain classes of separators. In cellophanic separators the growth is at many points and the dendrites are relatively broad, whereas in the membranes with filler, usually only a few points are penetrated and the dendrites are thin and hardly noticeable.

One purpose of this work was to reproduce the curve as given by Dalin and Solomon on page 41 of the stated reference. This curve represents the charge in coulombs necessary for dendrite penetration as a function of current density. The curve shows a quite sharp minimum. The current density at the minimum is recommended to be used for evaluation of the membranes. However, if this value is used, due to the steepness of the function at low current densities, a small deviation in current density could give a large deviation in the number of coulombs necessary for penetrating the membrane. Dalin and Solomon also state that the fact that this curve shows a minimum is significant to the probable shorting mechanism. It was therefore desirable to repeat similar measurements without and with a separator in order to evaluate the relation obtained.

It could be postulated that, as a first approximation, the number of coulombs/cm² necessary to produce a deposit which will reach the sensing electrode should be constant, regardless of the current density. Since only a certain space between cathode and sensing electrode has to be filled with

the zinc, the amount should be expressed by $It/cm^2 = k$. That such a relation will not be realized stems from the known fact that the nature of the electrodeposited zinc, especially the habits of the dendritic growth, depends on current density. It was also observed that, probably due to density changes in the electrolyte, considerable more deposit is formed at the bottom of the small cell ($3/4$ " diameter) than at the top, resulting in a quite uneven deposition. There might also be other reasons. For example, the nature of the zinc surface at the start of deposition will influence the time for the zinc growth to reach the platinum gauze.

The experimental values found, for the cell with only low density glass fiber felt as a spacer, are represented by the open circles in Fig. 15. The dashed curve represents the relation It/cm^2 drawn through the point at 25 mA/cm^2 . It can be seen that this relation seems to hold at low current densities and again at higher current densities. High current densities where an excess of hydrogen evolution is involved were not employed. Considerable deviation was observed around 15 mA/cm^2 . No interpretation of such a behavior will be given because duplicate runs show such a large scatter in the values, that many more points would be needed to gain any confidence in the results. The only relation indicated is that at high current densities a shorter time is needed than at low current densities to develop a bridge between cathode and sensing electrode. The fact that it requires only one dendrite to grow faster than the rest of the deposit, and since this growth seems to be rather unpredictable at present, a very large number of duplicate runs evaluated statistically would be necessary.

The same experiments were performed with a separator interposed. The separator was from a commercial silver-zinc battery. The result is shown by the solid circles in the graph. It can be clearly seen that the separator seems to have an influence, prolonging the time of developing shorts at low and higher current densities. The time necessary to penetrate the membrane between 10 mA/cm^2 and 20 mA/cm^2 does not differ substantially from the blank. But again, the statistical nature of such measurements must be considered. It would be premature to interpret the result.

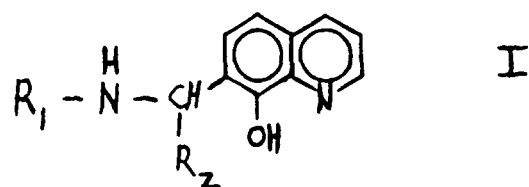
The separators produced by water extraction of a filler and polysulfone as a binder were tested and are indicated on the graph at a current density of 20 mA/cm^2 . The points are scattered between the two previous curves. This would indicate that no drastic retardation of dendritic growth through these separators can be expected.

Some results were also obtained on a smaller cell of only 1 cm^2 area with 10 mil spacing between cathode and separator. These results showed again considerable scatter and were given in the monthly reports.

Appendix II describes other experiments related to dendrite formation.

4. RESINS CONTAINING BONDED CHELATING GROUPS

Emphasis, in this phase of the work, has continued to be on resins prepared from the 8-hydroxyquinoline derivatives I with commercial epoxy resin formulations. In the cured resin, linkage of the derivatives I to the resin matrix is through the side chain secondary amine grouping of I. Since



the chelating agents I contain only a single secondary nitrogen, they are not efficient cross linking agents. We have, therefore, found it necessary to add, in addition, m-phenylenediamine in order to obtain proper curing with the commercial Shell formulation, Epon 826.

We have prepared two series of resins derived from the compounds I, which differ from each other in the relative amounts of I and m-phenylenediamine employed. In Table V we list the derivatives I used, together with the reaction conditions. Except as noted, good hard resins were obtained in each case after curing at 135°C.

Each of the resins listed in Table V was tested for resistance to chemical attack in 40% aqueous KOH at 135°C for 60 hrs. Samples were in the form of relatively thin flat fragments as obtained directly from the preparations. Weight loss after the treatment with KOH was taken as the criterion of stability, along with visible inspection. Weight change data are listed in Table V. Most of the resins did not suffer obvious visible deterioration as a result of this treatment. In general, weight gains, rather than weight losses, were observed. We attribute these weight gains, at least in part, to the replacement of free phenolic groups (derived from I) in the resin by potassium cations, together with hydration of the resulting potassium salt groupings. Most of the resins of Table V appear to be sufficiently resistant to attack by aqueous KOH to be used for battery separator applications.

Some effort has been devoted to attempts to establish the presence of metal-binding capacity in some of the resins derived from the 8-hydroxyquinoline derivatives I. In the first series of experiments, a 200 mg sample of each resin (reduced to a coarse powder) was allowed to stand for one week, with occasional shaking, in a solution prepared from 0.20 g cupric acetate monohydrate, 50 ml water, and a drop of liquid Aquet detergent, as wetting agent. The resulting solution (without resin) had a pH of 5.7. At the end of one week the solid was filtered off and washed with water. The crucible was then ignited at 800°C to convert any copper content of the resin to CuO. For each of the six resins investigated (Table VI), negligible residue was left after this treatment, indicating that no appreciable uptake of Cu^{2+} had taken place. A possible reason for this lack of reaction may be the relatively low pH of the reaction mixture, since the parent compounds I are, themselves, known to require relatively high pH values in order to chelate with metal ions. Further runs of this type, employing solutions of higher pH, are planned if time allows.

In a second series of runs the availability of the phenolic groups in the resin (derived from I) to ionization was investigated, since this is a prerequisite to chelation with metal ions. For this purpose, each 100 mg sample of powdered resin was allowed to stand overnight, at room temperature, with a mixture of 2.00 ml of 0.100 M aqueous NaOH and 50 ml water. The solid was then filtered off on sintered glass and washed with water. The filtrate (plus washings) was titrated with 0.02 M aqueous HCl to establish the amount of NaOH consumed by the resin. A glass-calomel electrode pair and pH meter were used to follow the course of the titration. Results are expressed in Table VI as moles of OH^- consumed per mole of oxine derivative I present in the resin. (There was no conclusive evidence from the titration curves for the extraction of soluble acidic materials into the aqueous phase.)

For the compounds investigated (Table VI), the maximum possible value of the ratio (OH^- consumed/cmpd I) is unity except for the first resin listed, where a value of 2 is possible, because of the additional presence of the carboxyl group. The values of the ratio observed (Table VI) are in all instances less than 20% of these values. This may be due to several reasons, including (a) interaction of a portion of the phenolic groups with the reaction mixture during the preparation of the resin, and (b) lack of complete penetration of the sodium hydroxide solution into the interior of the resin particles. The results do indicate, however, that a significant fraction of the phenolic groups in the cured resin remain available for further interaction with metal cations.

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APPENDIX I

SIMPLIFIED D.C. RESISTIVITY TESTER

Some of the experimental films had such a high resistance that they could not be measured by either the d.c. or a.c. tests described in the previous report. In order to know the direction to go in the fabrication of such films, some resistance values were desirable. It was therefore decided to construct a simple, direct reading resistivity tester which would measure quickly without balancing a bridge circuit.

The simplified tester is a modified version of the d.c. tester without the reference cells. The tester indicates the resistance by the measured potential across a cell when a current is flowing between the electrodes. In order to avoid polarization of the electrodes when passing current, they were made of half-charged sintered cadmium plates, so that when one electrode is charged the other is discharged. The two cadmium electrodes were positioned quite close to each other to minimize the background resistance. The test circuit consisted of a battery, variable resistance, voltmeter and a milliammeter. On setting the current at 10 ma, each volt on the meter corresponds to a resistance of 100 ohms, so that an estimate of the film resistance can be obtained rather quickly. A setting of 1 ma was used for very high resistance films. This method seems precise enough to decide if the films should be evaluated further with the more sensitive testers.

The importance of proper presoaking of the film in 40% KOH for an appreciable length of time was more easily noticed with this device. For example, if a water-wet film was introduced and a reading in the 1000 ohm range was obtained, a low stable value was not reached for several hours. Also, even films which were presoaked for a day or longer in 40% KOH showed a decline in resistance after several minutes in the tester. For some films this drift was quite long. The effect of pressure was discussed above.

APPENDIX II

THE EFFECT OF ELECTRODE ROTATION ON
DENDRITIC GROWTH OF ZINC

Among the methods used to reduce the effects of zinc dendrite growth are:

- (1) Controlled charging
 - a) Low current density charging
 - b) Intermittant charging
 - c) Reverse charging
- (2) Additives to electrolyte
 - a) Organic
 - b) Inorganic
 - c) Alloying of electrode (Hg)
- (3) Mechanical movement of electrolyte or electrode
 - a) Stirring of electrolyte
 - b) Ultrasonic vibration of assembly
 - c) Rotation or vibration of electrode
- (4) Interposition of a proper separator between the electrodes, confining the dendrites to the zinc compartment.

Some time ago experiments were conducted to suppress dendrite growth by some of the schemes indicated above. Most of the work was concentrated on the use of additives. Although a number of these had a beneficial effect, it is doubtful if many would survive a sterilizing environment since they were mostly of the organic type. Of the inorganics, Pb, Sn, Al and Na_2SiO_3 had the ability to retard dendritic growth, but their overall effect on a battery performance was not proven. Similar claims have since appeared in the literature (Annual Power Sources Conference, Atlantic City, N.J., 1966).

Mechanical movement, for example magnetically rotating a Teflon covered iron bar directly on the zinc electrode, did not prevent the formation of dendrites. Application of ultrasonic vibration over a broad frequency range was relatively ineffective under the conditions tested. Also controlled charging seemed of very limited use. It was therefore surprising that recently it has been reported that dendrite growth is suppressed by electrode rotation.* This scheme had not been tried because it seemed entirely impractical in battery construction. However, because of its theoretical implication as to the causes of dendritic growth, and in order to evaluate the effect of rotation, the following experiments were conducted at this time.

A zinc disc of 1.5 cm diameter (7.0 cm^2) was rotated at different speeds (0-500 rpm) in 40% KOH saturated with zinc oxide at room temperature. The instrument was described under the heading: Ag Diffusion in a previous monthly report. A somewhat larger and heavier zinc counter-electrode was located $3/4$ " from the rotating disc in the present work.

To avoid the performance of many experiments at different current densities, a single value was chosen. This caused noticeable gas evolution from the electrode while stopped. The tests were run for $1/2$ hr. at $2 \text{ A} \pm 0.1$, while regulating the current manually. The current density was therefore in the neighborhood of 0.28 A/cm^2 , although regulation was not too effective and fluctuations occurred. The ability to brush away the deposit with a short stiff bristle brush was used as a test for adherence.

On a non-rotating electrode, a non-adherent mossy precipitate was formed. No substantial difference was noticed at 50 rpm. At 100 rpm, the deposit was firmer, but still could be brushed away over the whole surface. The ratio of zinc brushed away to the total zinc deposited, as determined by weighing the electrode before and after deposition and after scraping, was considered dendritic growth.

*Yardney Electric Corporation, Report on Contract No. NAS5-3873 (1964).

At 100 rpm, 85% was still dendritic. The deposit became quite adherent at 200 rpm, but not smooth. Some holes were present, extending to the base zinc. Protrusions were observed on the surface. Under the microscope the deposit looked like an interwoven forest of individual dendrites. Most of the material that could be brushed off was located around the edge, where the deposit was higher. The porosity of the deposit was indicated by the fact that, after washing in water and acetone, the sample started to gain weight on the balance. It was noticed that the plaque heated up and in a short time converted to zinc oxide. At 300 rpm, an even denser structure was obtained, with only a few dense dendrites at the periphery, 12% being dislodged. No material could be brushed away at 500 rpm, indicating the formation of a quite dense structure. The results are indicated graphically in Figure 16. It is clearly shown that the rotation of the electrode has indeed a pronounced effect, and that dendritic growth has a direct bearing on the diffusion layer, notably its thickness, in planar diffusion. The rotating disc electrode seems to emerge as a new tool in electro-crystallization studies.

Because, as stated earlier, the practical applications of rotation in a storage battery are not too obvious, although not impossible, this approach was not pursued further.

Table I

Filler Concentration and Characteristics of Experimental Membranes
(Filler makes up the major portion of the polymer-filler wgt.)

Support/Binder	Filler	Thickness mils	% Polymer + Filler by wgt.	Electrical Resistivity (ohm-cm)	Remarks
Webril/Polysulfone	None	2.2	13	727.7	--
"	ZrO	3.7	60	140.4	--
"	ZrO	5.6	27	218.6	--
Webril/Polysulfone	TiO ₂	2.0	42	565.4	--
"	TiO ₂	3.8	33	143.1	--
"	TiO ₂	5.1	63	350.3	--
Webril/Polysulfone	TiO ₂	3.8	34	52.0	--
"	TiO ₂	3.1	14	311.0	--
"	TiO ₂	3.2	4.5	127.3	--
3 sheets Webril/Polysulfone	CaO	6.2	54	58.0	--
2 sheets "	CaO	5.5	70	130.5	--
1 sheet "	CaO	2.8	66	57.3	--

(Continued)

Table I (Continued)

Support/Binder	Filler	Thickness mils	% Polymer + Filler by wgt.	Electrical Resistivity (ohm-cm)	Remarks
Webril/Phenoxy	ZrO	5.4	23	319.7	Oven baked
"	ZrO	5.5	31	438.3	"
"	ZrO	4.0	50	230.4	"
Webril/Polysulfone	Polyethylene Oxide (Extracted)	4.7	26	104.8	
Webril/Polysulfone	Linde 5A	7.5	--	34.2	All samples approximately 50% by wgt. (Filler + polymer)
"	Linde 4A	7.0	--	53.1	
"	Linde 3A	6.1	--	72.2	
"	Linde 13X	6.6	--	60.9	
"	Zeolon	5.9	--	30.4	Oven baked

Table II

Polymer Composite Evaluation - One Cycle 60 Hr. -40% KOH-135°C

Material	As Cast	One Cycle
Unsupported film with 0.05 g $Zr(OH)_4$ as filler. Polymer soln. - $\frac{10 \text{ g polysulfone}}{100 \text{ ml DMAC}}$	White film 4 mil tk.	No measurable change
" " $\frac{15 \text{ g phenoxy}}{100 \text{ ml DMAC}}$	White film 4.5 mil tk.	Film badly distorted and yellowed. 3.3 mil tk.
" " $\frac{10 \text{ g polyvinylidene fluoride}}{100 \text{ ml DMAC}}$	White film 5.9 mil tk.	Brittle brown film.
Supported 5 mil Webril. No filler. $\frac{10 \text{ g polysulfone}}{100 \text{ ml DMAC}}$	White coating 6.6 mil tk.	No measurable change.
" " $\frac{15 \text{ g phenoxy}}{100 \text{ ml DMAC}}$	White coating 6.8 mil tk.	Slightly yellowed Composite. 9 mil tk.
" " $\frac{10 \text{ g polyvinylidene fluoride}}{100 \text{ ml DMAC}}$	White coating 6.6 mil tk.	Composite covered with dusty brown powder. 6.8 mil tk.
Webril supported, 0.5 g titanium oxide filler, 1 ml of 5 g phenylene oxide in 100 ml toluene.	White film 5.8 mil tk.	Powdery; brittle
Same with no filler.	5.8 mil	Powdery; brittle

Table III

Cycled Water-Precipitated Membranes, Dried

Material	Conditions	% Weight Change
Polysulfone, 15 g/100 ml DMAC	Cycled 60 hr-40% KOH-135°C. Dried, 1 hr. 110°C.	-1.3
"	"	-2.5
"	"	-1.1
"	"	-1.4
Polysulfone, 15 g/100 ml DMAC + 5 g titanic oxide	"	-21.6
Polysulfone, 15 g/100 ml DMAC + 5 g Zeolon H	"	-25.0
Polysulfone, 15 g/100 ml DMAC + 5 g Zr(OH) ₄	"	-21.5
" (Duplicate)	"	-21.9
Polysulfone, 15 g/100 ml DMAC + 5 g Linde 10X molecular sieve	"	-24.9
" (Duplicate)	"	-24.6

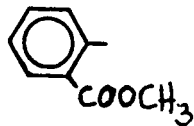


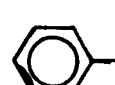
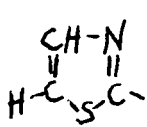
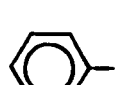
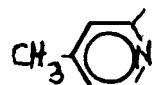
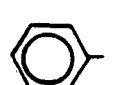
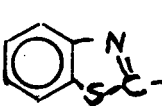

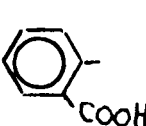
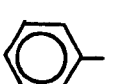
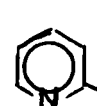
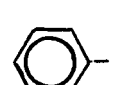
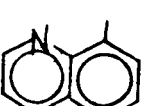
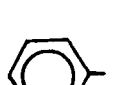
Table IV

Cycled and uncycled Water Precipitated Membranes Fired 2 hr, 660°C

	Material	Conditions	% Weight Material Remaining
	Polysulfone, 15 g/100 ml DMAC, 5 g Zr(OH) ₄	Sample air dried for 1 hr. at 110°C. Weighed, then fired.	18.2
	" Duplicate	"	20.5
<u>Cycled</u>	Polysulfone, 15 g/100 ml DMAC, 5 g Zr(OH) ₄	" Cycled weight compared to fired weight	4.3
<u>Cycled</u>	" Duplicate	"	1.2
	Polysulfone, 15 g/100 ml DMAC, 5 g Linde molecular sieve	" Sample air dried 1 hr, 110°C. Weighed, then fired.	23.8
	" Duplicate	"	20.0
<u>Cycled</u>	Polysulfone, 15 g/100 ml DMAC, 5 g Linde molecular sieve	" Sample air dried 110°C. Weighed, then fired-cycled weight compared to fired weight.	0.5
<u>Cycled</u>	" Duplicate	"	1.0
	Polysulfone, 15 g/100 ml DMAC, no filler	" Sample air dried 1 hr. 110°C. Weighed, then fired.	<0.05
	" Duplicate	"	<0.05
	Polysulfone, 15 g/100 ml DMAC, no filler	Cast in water (1 hr). Air dried 1 hr, 110°C, 1 hr. Then fired to meas. ball mill pickup.	0.41
	Ball milled for 16 hours		0.42
	"	"	0.46

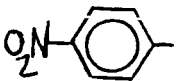
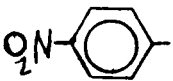
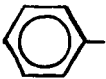
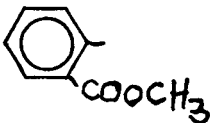


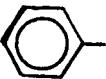
Table V

Epoxy Resins Containing 8-Hydroxyquinoline Groupings^a

8-Hydroxyquinoline precursor		Wt. used (grams)	% wt. increase after exposure to KOH solution at 135°C
<u>R₁</u>	<u>R₂</u>		
		0.96 0.48	1.8 0.64
		0.82 0.40	0.23 0.68
		0.83 ^c 0.41	12.8 5.2
		0.85 0.43	0.60 1.5
		0.96 0.48	6.3 3.3
		0.93 0.46	b 6.6
		0.82 0.41	-0.13 0.48
		0.94 0.47	0.48 0.23

(Continued)

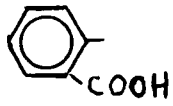
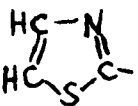

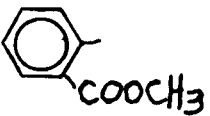
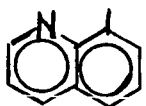
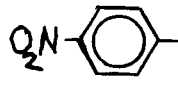
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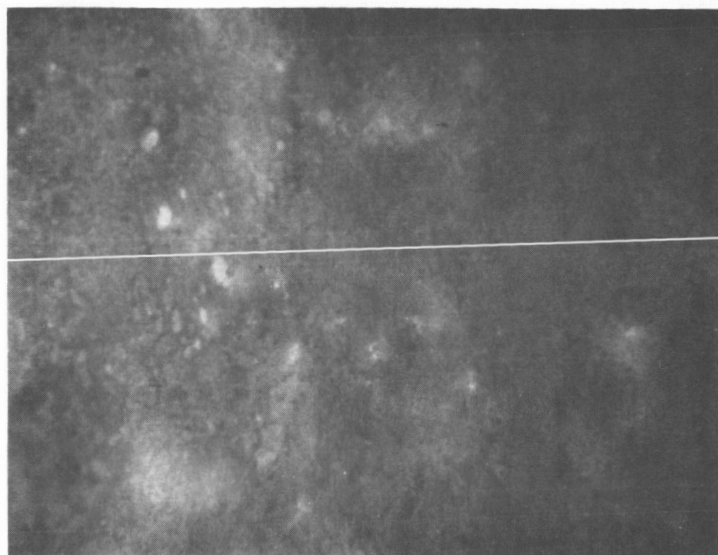
8-Hydroxyquinoline precursor		Wt. used (grams)	% wt. increase after exposure to KOH solution at 135°C
<u>R₁</u>	<u>R₂</u>		
	$\text{CH}_3\text{CH}_2\text{CH}_2-$	0.84 0.42	-40.4, -24.1 ^b -0.34
		0.93 0.46	0.26 0.64
		0.96 0.38	-5.7 2.8
		0.86 0.43	2.3 0.83

-
- a. Resins were prepared from 0.92 grams Shell Epon 826 and 0.134 grams m-phenylenediamine. Curing conditions were 6 hours at 140°C, except as noted.
- b. The product from this reaction mixture did not give a coherent resin. It was not tested further.
- c. Curing temperature 150°C.

Table VI

Interaction of epoxy resins derived from oxine derivatives
with copper acetate or with NaOH

8-Hydroxyquinoline precursor			
<u>R₁</u>	<u>R₂</u>	<u>Tested with copper acetate</u>	<u>Moles OH⁻ consumed per mole of oxine precursor</u>
	phenyl	yes	0.35
	phenyl	no	0.13
	phenyl	yes	0.16
	phenyl	yes	0.15
phenyl	phenyl	yes	not tested
	phenyl	yes	not tested
	phenyl	yes	not tested

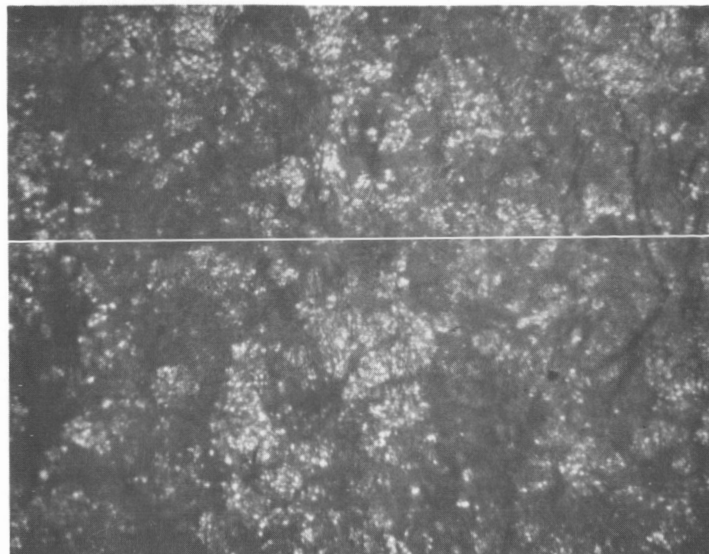


Transmitted Light 22X



Reflected Light 22X

Fig. 1. Sample No. 58-9-27-1. Polysulfone polymer binder, $\text{Zr}(\text{OH})_4$ filler, 2 layers 1.5 mil each thick, Polypropylene Webril.



Transmitted Light 22X



Reflected Light 22X

Fig. 2. Sample 103-9-29-1. Phenoxy polymer binder, $\text{Zr}(\text{OH})_4$ filler, 3 layers 1.5 mil each thick, Polypropylene Webril.



Coating Polymer Solution on Glass Plate
Using Gardner Applicator

FIGURE 3



Water Precipitation of Polymer Solutions

FIGURE 4

Curve 579751-A

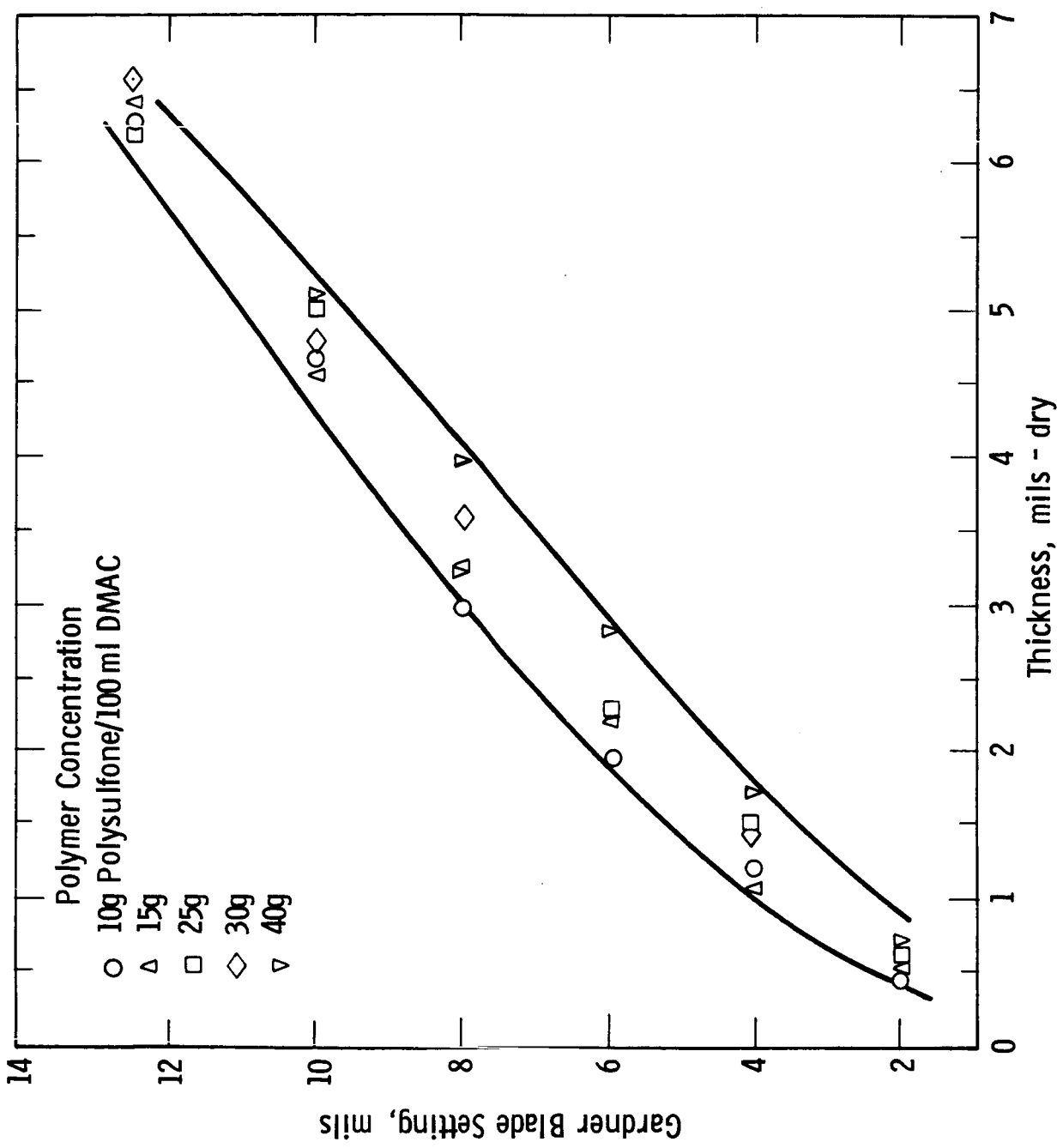
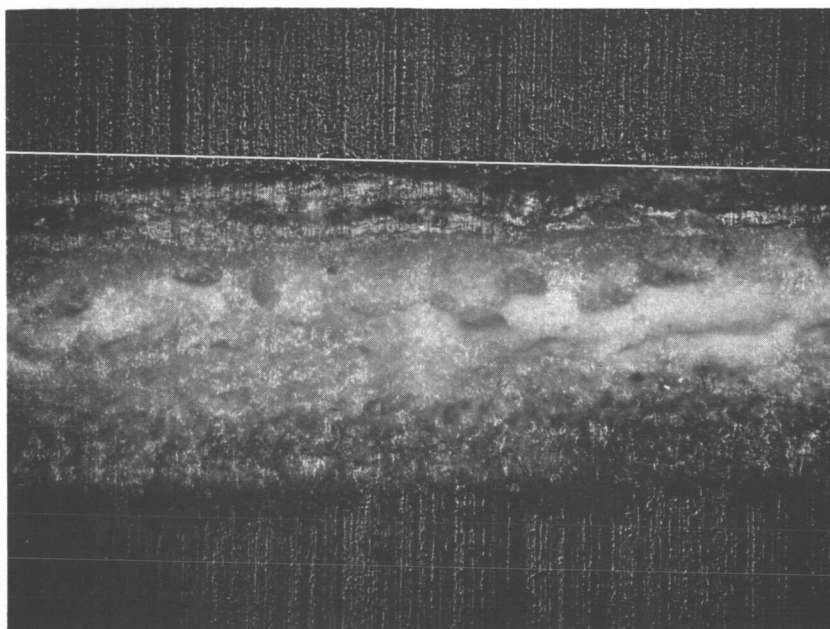
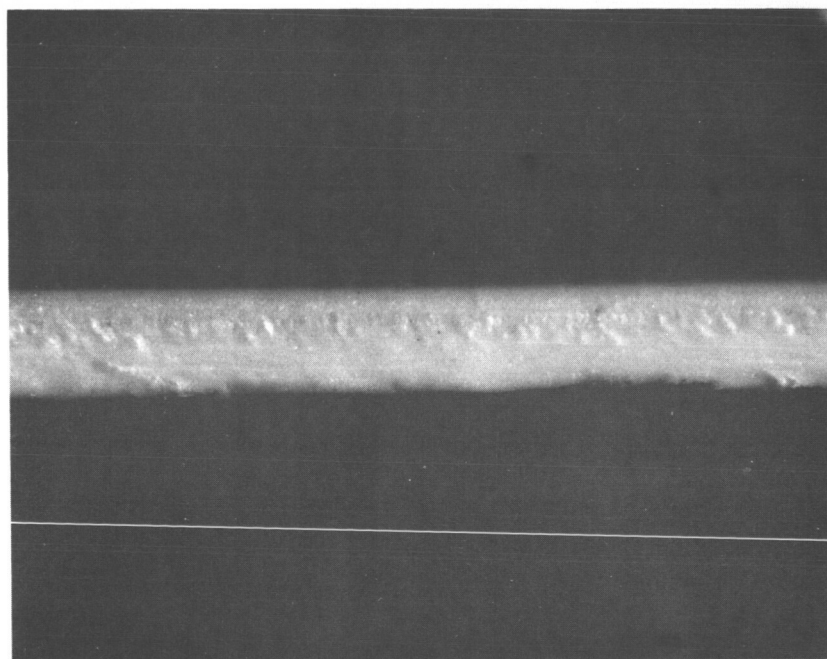


Fig. 5—Blade setting vs dry film thickness for various polymer concentrations



200 X



100 X

Cross Sections of Membrane 83-11-17-2
6.3 mil tk. water cast
Polysulfone without filler

FIGURE 6

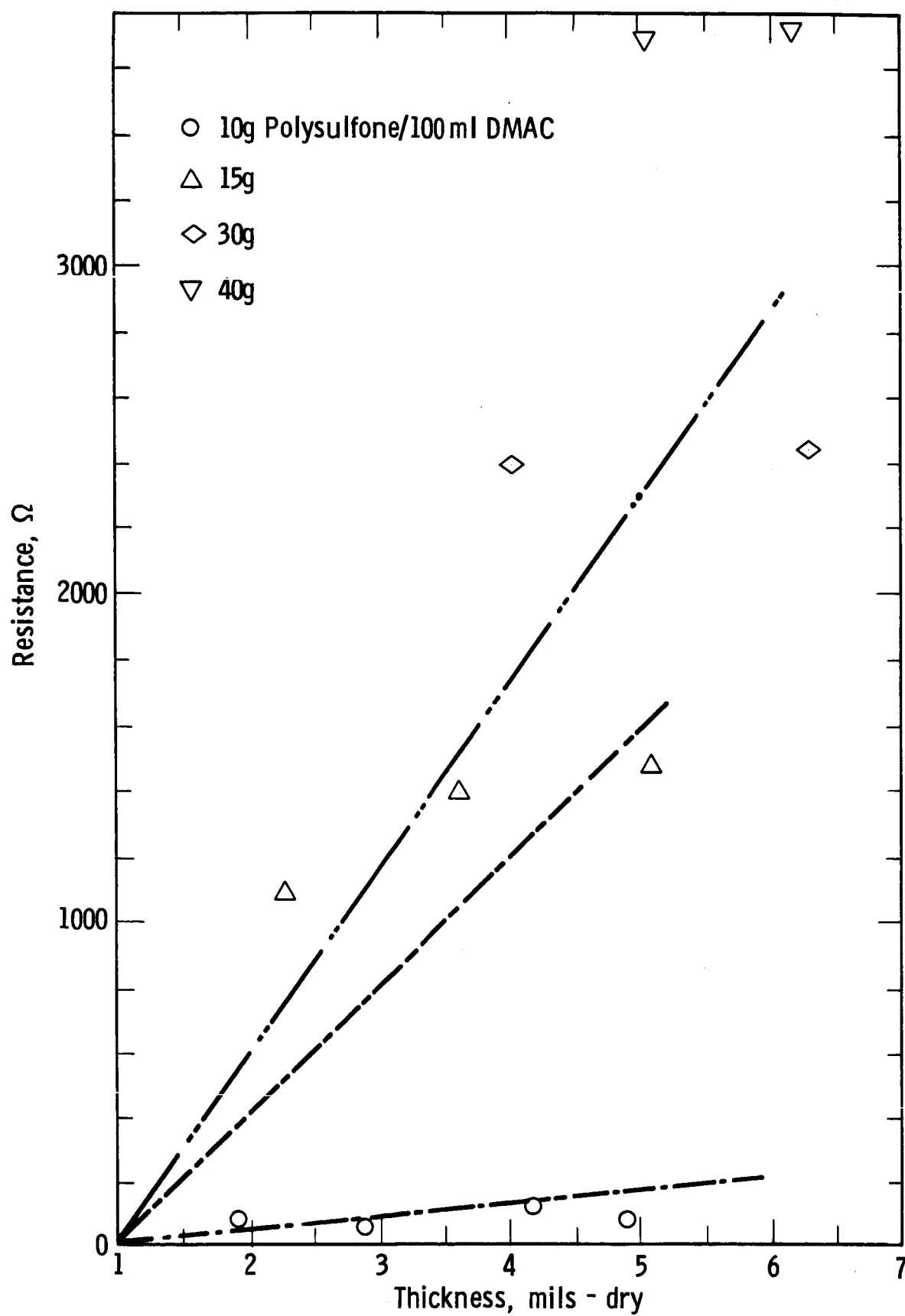


Fig. 7—Resistance vs film thickness for various polymer concentrations

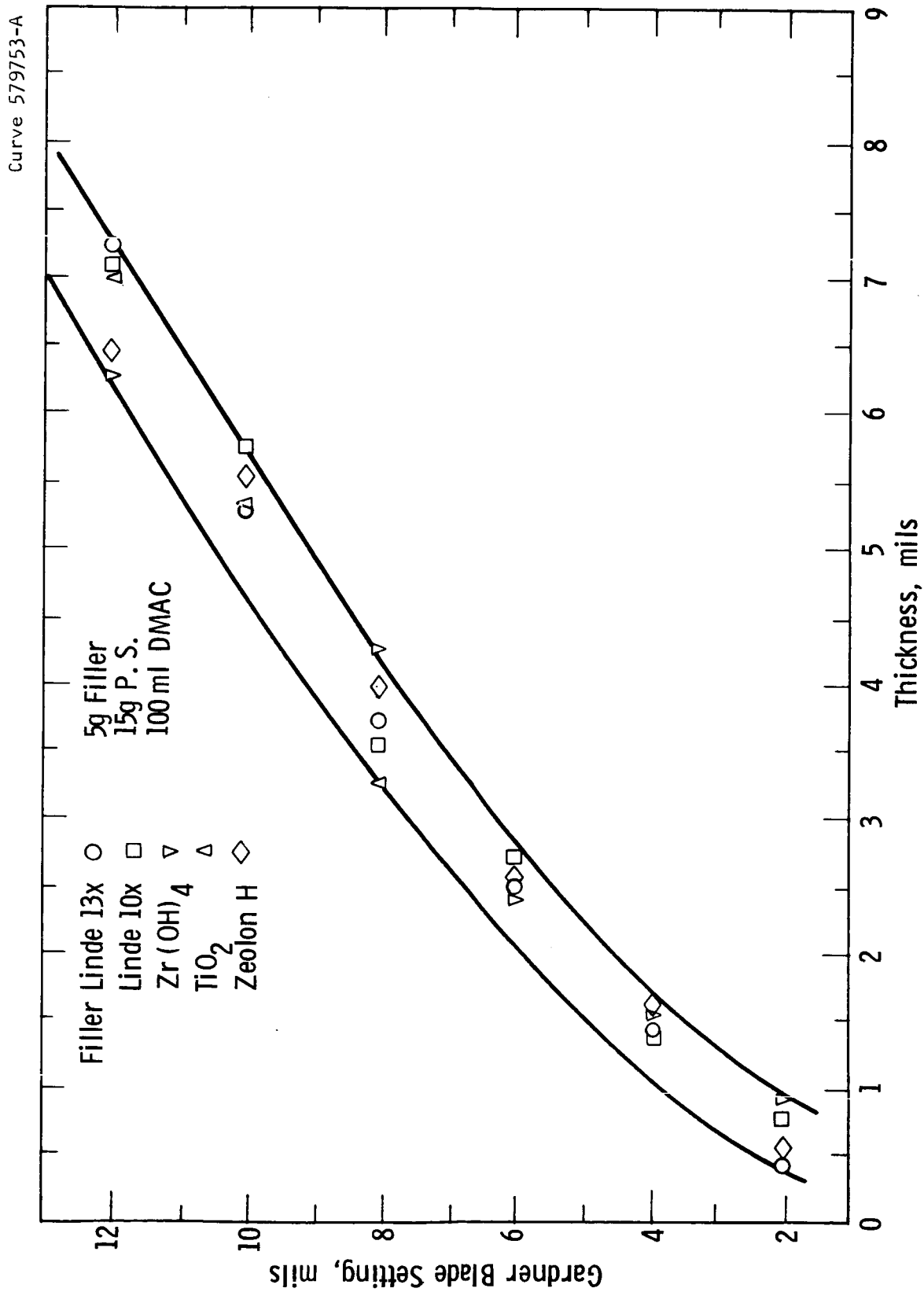


Fig. 8—Blade setting vs dry film thickness with different fillers

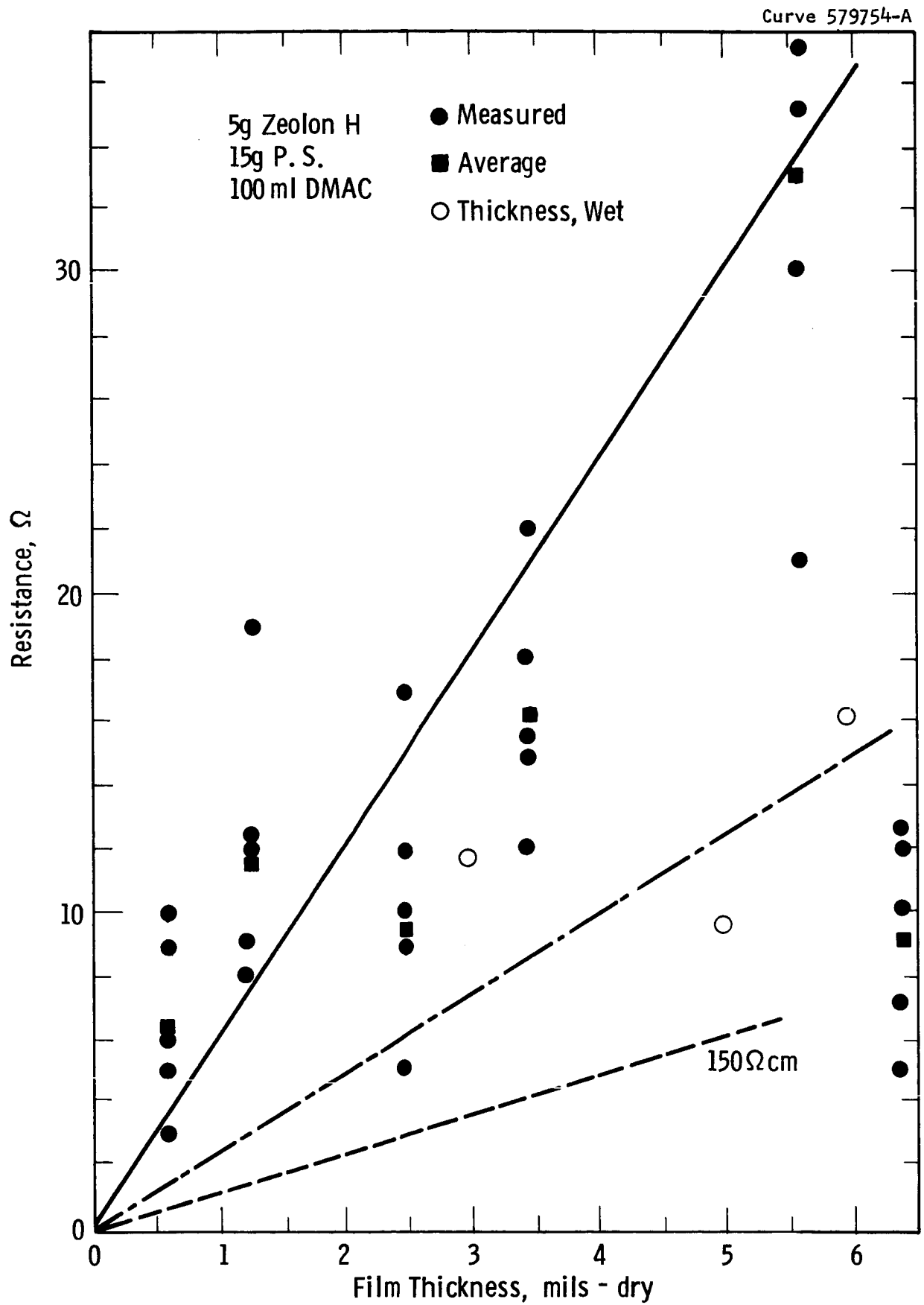


Fig. 9—Resistance vs film thickness with Zeolon H as fillers

Curve 579755-A

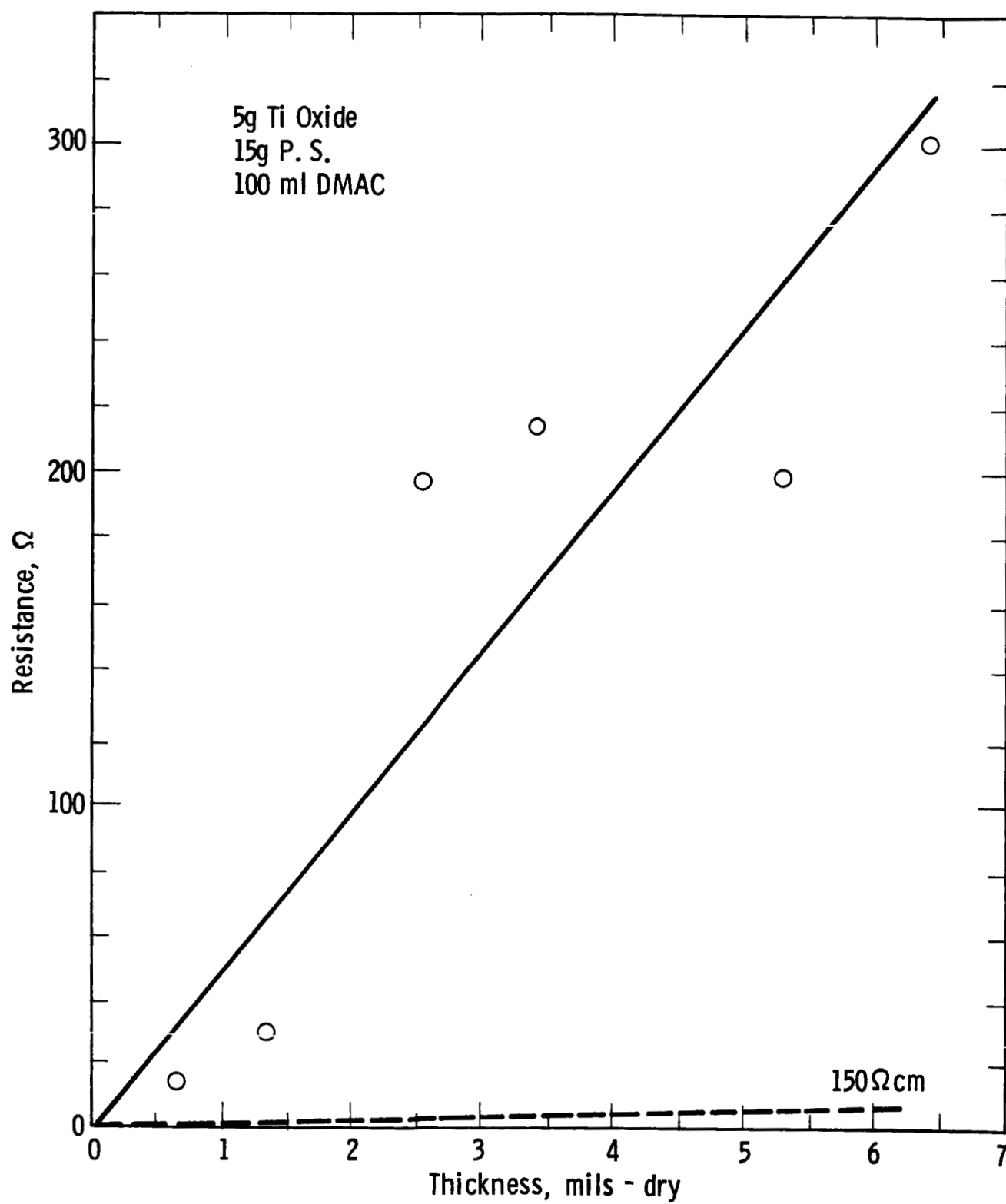


Fig. 10—Resistance vs film thickness with Ti oxide as filler

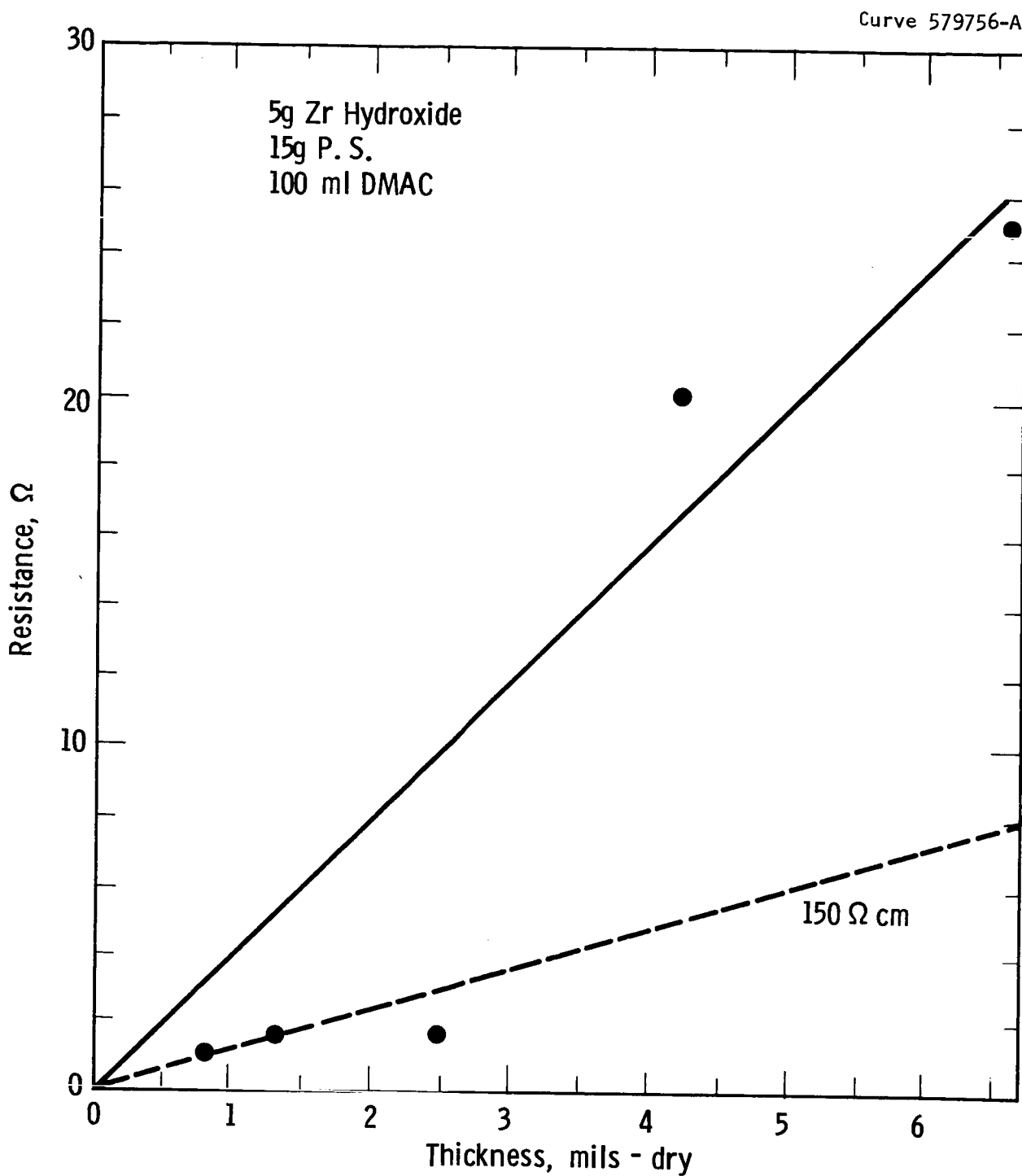
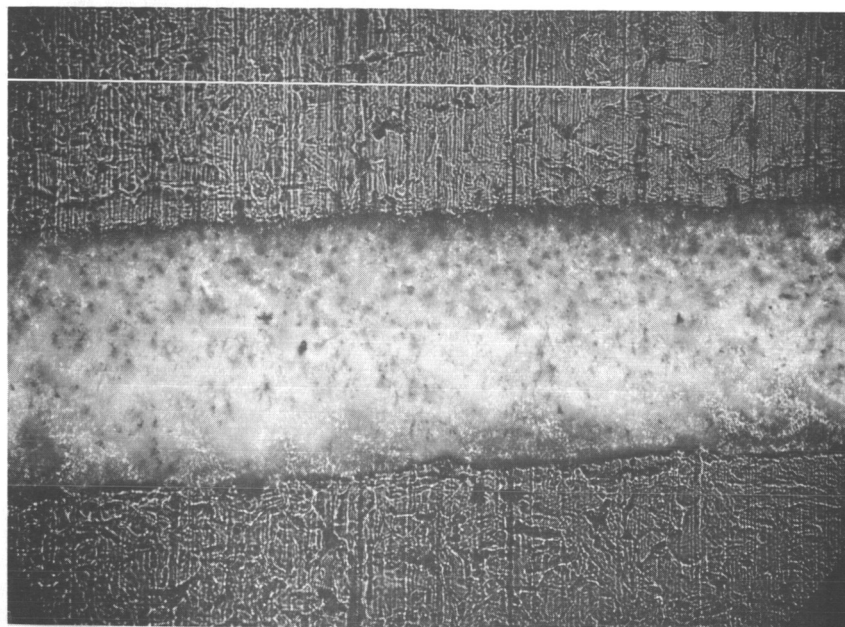
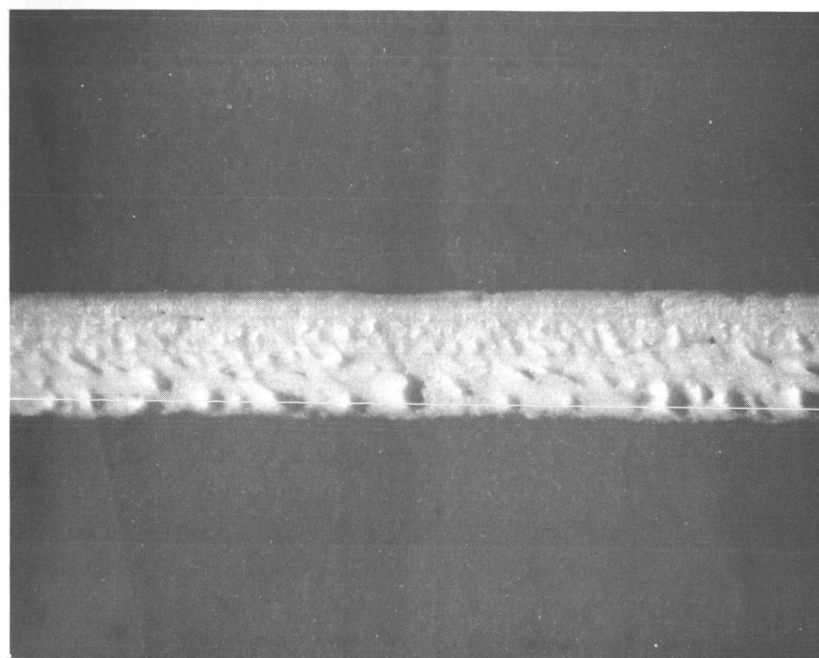


Fig. 11—Resistance vs film thickness zirconium hydroxide as filler



200 X



100 X

Cross Sections of Membrane 87-11-29-3
 6.3 mil tk. water cast
 Polysulfone with 25% filler by weight ($\text{Zr}(\text{OH})_4$)

Figure 12

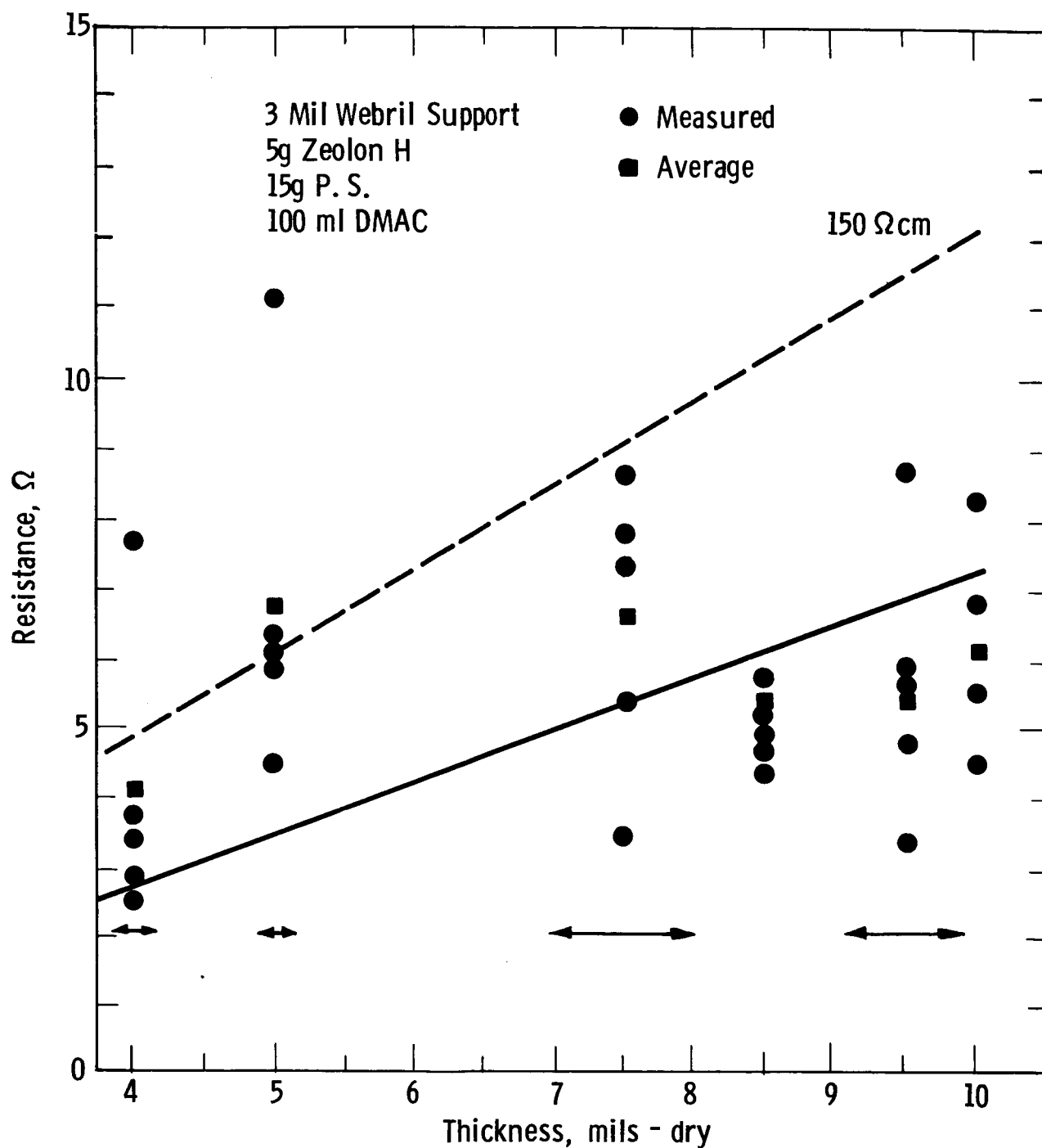


Fig. 13—Resistance vs film thickness with zeolon H as filler on Webril

Dwg. 852A909

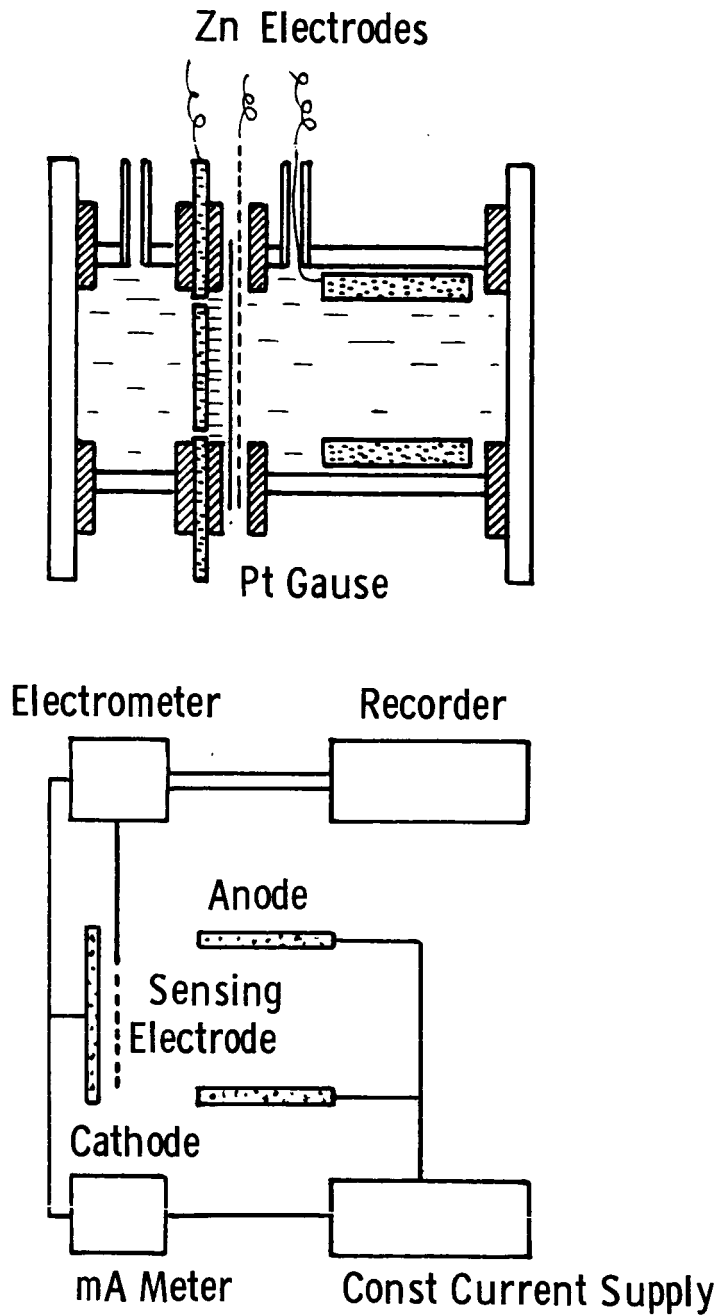


Fig. 14—Dendrite penetration tester

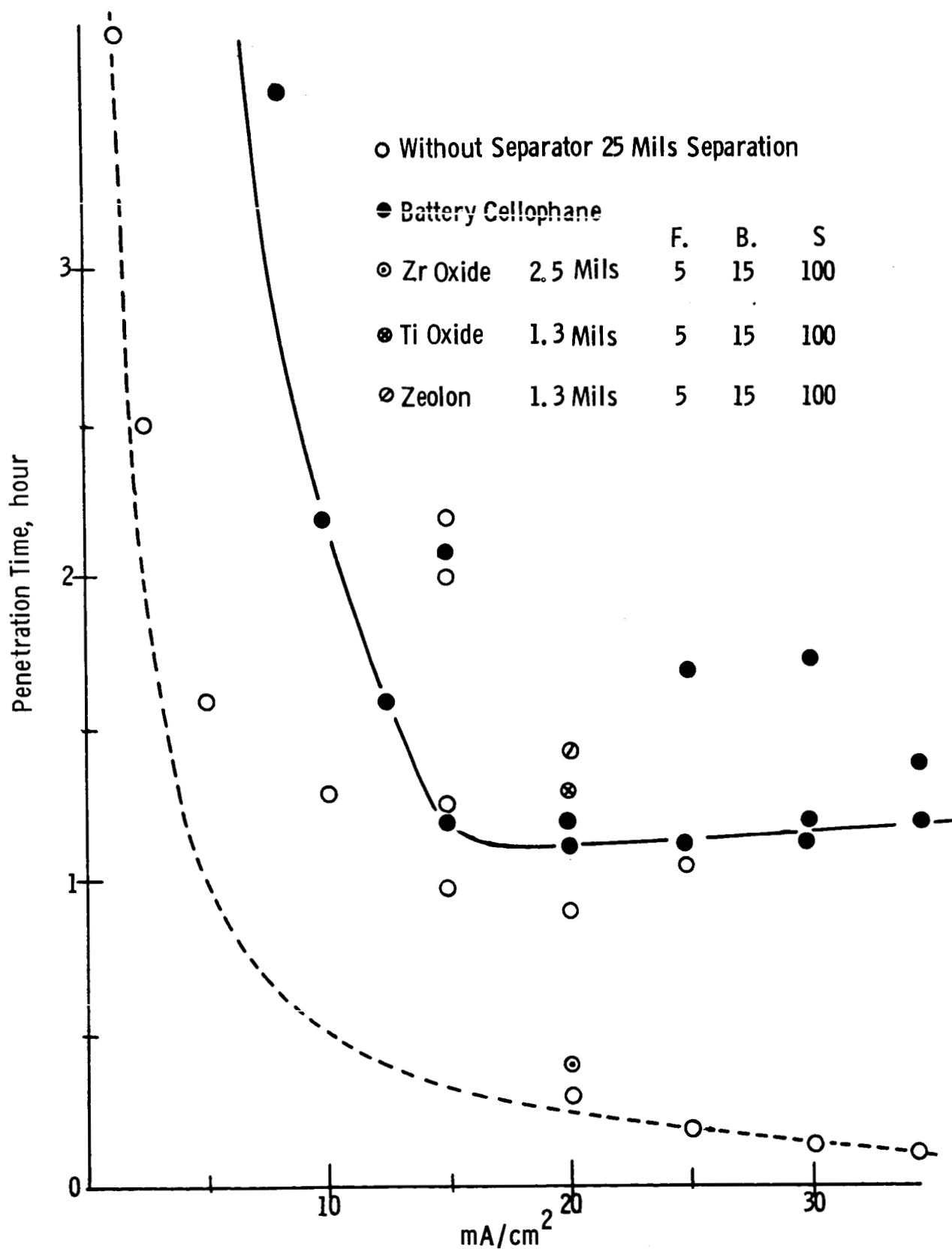


Fig. 15—Dendrite penetration time - current density relations

Curve 579871-A

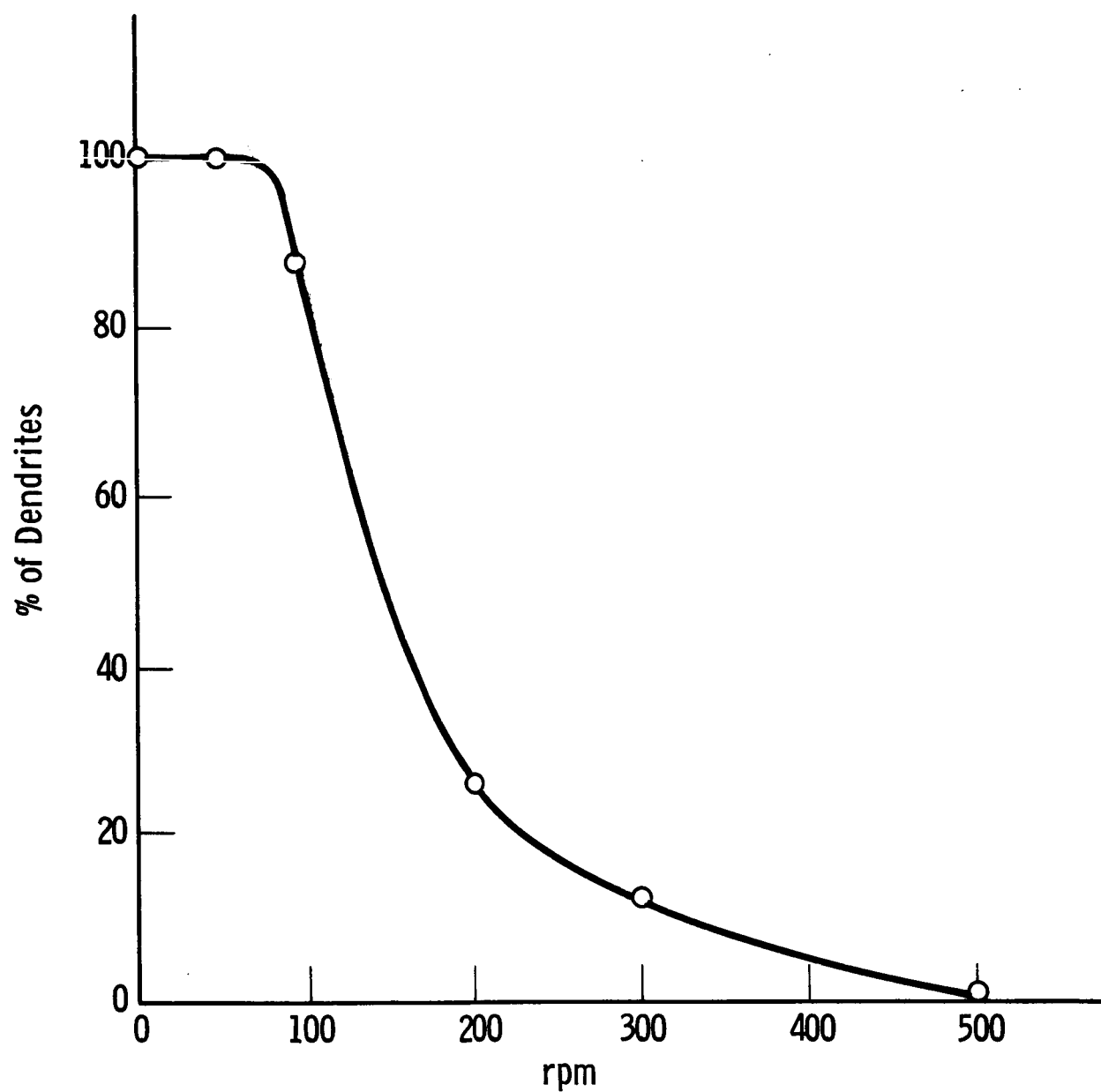


Fig. 16—Dependence of adherent growth on rotation of zinc disc electrode